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A STUDY OF AMMONIA DESORPTION FROM ZEOLITE BY TG/FTIR

by

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ABSTRACT

The thermal decomposition of ammonia-loaded zeolite was studied by simultaneous thermogravimetry (TG)/Fourier Transform infrared spectroscopy (FTIR) in inert and oxidizing atmospheres. The results were compared with those of zeolite before loading. X-ray diffraction was used as supplementary technique. The rate of ammonia desorption was found to be dependent on the oxygen partial pressure. Traces of N_2O were detected in the effluent gas in presence of high partial pressures of oxygen.

Keywords: Thermal Analysis, Thermogravimetry, FTIR, TG/FTIR, Zeolite, Ammonia, Desorption

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INTRODUCTION

In the mining industry, ammonium nitrate-based explosives are often used to fracture the rock mass. Ultimately this leads to the accumulation of nitrogen bearing by-products, particularly ammonia, in the mine effluents. At present, the Mineral Sciences Laboratories of CANMET is undertaking a study on methods for the potential removal of ammonia from mine effluents. Zeolites have been used for many years for the adsorption of ammonia in the food industry, and may also be useful for the present application.

Samples of zeolite mineral as received, washed, and washed and loaded with ammonia were submitted for examination by TG/FTIR. The thermal behaviours of the three samples were studied in inert and oxidizing atmospheres up to 900°C. The purpose of the study was to examine the desorption trends during heating and to identify the gaseous species.

MATERIALS AND EXPERIMENTAL PROCEDURE

Three clinoptilolite zeolite samples were investigated by TG/FTIR; as received (-20+65 mesh), zeolite after washing with water (-16+20 mesh) and zeolite after washing with water and loading with NH_4Cl in an ion exchange column (-16+20 mesh). The samples (multi-colour: green, brown, beige and white) were used without grinding to avoid any physical changes that might influence the results.

A DuPont 9900TA system with a 951TGA module was used in the study. The thermobalance was interfaced with a BOMEN-MB100 Fourier transform infrared (FTIR) spectrometer with a Compaq 386/20e computer capable of simultaneous control of the balance and the spectrometer. In the spectrometer, a 10 cm long gas cell with standard KBr windows was used. The evolved-gas transfer line between the thermobalance and the spectrometer was made of a small-diameter glass tube connected to a glass filter for the removal of particulates from the gas stream. The TG and FTIR measurements were made simultaneously.

In the experiments ≃30 mg of sample were subjected to a programmed heating rate of 20°C/min up to 900°C in a quartz pan using 50 mL/min of purge gas. Three different atmospheres were used; pure He, He/O_2 (1:1) and pure O_2.

RESULTS AND DISCUSSION

An x-ray diffraction pattern of the "as received" zeolite is shown in Figure 1. The XRD pattern may be attributed to clinoptilolite and/or $Ca_{1.23}Al_2Si_7O_{18}.6H_2O$. When the sample was heated to 900°C in air (Figure 2) or in He (Figure 3), the XRD of the products showed a rounded baseline indicating the presence of an amorphous phase. The XRD pattern of the starting materials remained evident, in addition to an unidentified peak at 11.26 (D Space).

The weight loss results from the TG/FTIR diagrams are summarized in Table 1. It is noticeable that the weight loss detected with the "as received" zeolite is less in helium than that in presence of oxygen (reproducible). This indicates that a minor reaction (perhaps with an impurity) which is enhanced in presence of oxygen is taking place. The washed zeolite exhibited comparable weight losses in all atmospheres. Washing may have removed one or more impurity components that had reacted in presence of oxygen in the case of the "as received" sample. Somewhat higher weight losses were recorded in the case of the loaded zeolite. Although systematic, the differences in the weight loss may not be of major significance due to the inhomogeneity of the samples.

Table 1 - TG Weight Loss Up to 900°C

Zeolite Sample	% Weight Loss		
	He	He/O_2	O_2
as received	10.5 (repeat 10.2)	12.2	12.1
washed	12.5	11.8	12.2
washed and loaded	13.4	14.0	13.8

Figures 4 to 12 show the TG/FTIR diagrams of the three zeolite samples in He, He/O_2 (1:1) and pure oxygen. The diagrams include the weight loss and gas evolution profiles. The diagrams obtained in He/O_2 or pure oxygen atmospheres showed a marked cycling in heating during the water evolution up to 400°C. This phenomenon occurs due to the fact that the TG/FTIR system employs the sample thermocouple for controlling the TG furnace. In presence of air or oxygen, having much lower thermal conductivities than helium, a significant delay in the response of the heating element to the control thermocouple occurs, leading to the observed cycling. This phenomenon is not noticeable in helium.

Figures 4, 5 and 6 show the TG/FTIR diagrams of the "as received" zeolite in He, He/O_2 (1:1) and pure oxygen. Only H_2O and trace CO_2 evolved during heating. The water evolution peak maximum increases with the higher oxygen partial pressure. This may be a direct effect of the furnace cycling mentioned earlier, as shown by the multiple peaks during the water evolution in Figures 5 and 6. Similar trends appeared for the washed zeolite, Figures 7, 8 and 9.

The TG/FTIR diagrams of the washed and NH_3-loaded zeolite are shown as Figures 10, 11 and 12. The water evolution slightly increases with the higher oxygen partial pressure in the gas. Traces of CO_2 were also detected. The loaded zeolite showed less water evolution and less weight loss due to water than the "washed only" zeolite run in the same atmosphere.

The ammonia evolution peak maximum was found to increase with the addition of oxygen to helium but no further increase was noticed in pure oxygen. The temperature range of ammonia desorption is significantly reduced by the addition of oxygen to the purge gas. When the NH_3-loaded zeolite is heated in helium (Figure 10) the ammonia evolved in the temperature range 200 - 800°C. Water also evolved at about 700°C. With the addition of oxygen to helium (Figure 11), the ammonia evolution was complete around 650°C.

Traces of N_2O were detected near the end of the NH_3 desorption. An infrared spectrum of nitrous oxide (N_2O) with other species evolved at 550°C is shown in Figure 13.

When the loaded zeolite was examined in pure oxygen (Figure 12), the ammonia evolution was complete around 600°C. Two other water evolution peaks appeared at 600 and 740°C. The amount of N_2O evolution, although still minor, has increased from the 50% oxygen experiment. The loaded zeolite was also heated in dry air. The TG/FTIR diagram is shown as Figure 14. The experimental results are similar to the 50% oxygen in helium experiment but without the evolution of nitrous oxide.

The presence and amount of nitrous oxide in the effluent gas seem to be dependent on the oxygen partial pressure. Prideaux and Lambourne [1] reported that the combustion of ammonia in oxygen is a complex process but may be represented by the following reaction:

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O \qquad (1)$$

They also reported that, in an oxygen deficient atmosphere, hydrogen may form, while, in excess oxygen, nitrogen oxides form. Wendlandt [2] reported that, in the catalytic oxidation of ammonia, nitrous oxide may form by the following reactions:

$$NH_3 + O_2 = HNO + H_2O \qquad (2)$$

$$2HNO = N_2O + H_2O \qquad (3)$$

The water evolution occurring near the end of the NH_3 desorption, shown in Figures 10, 11 and 12, may be due to reaction 1. Tsitsishvili et al.[3] studied the thermal properties of modified zeolites, and found that the zeolite deammoniation process is accompanied by the formation of hydroxyl groups, which are gradually removed from the zeolite structure as the temperature rises. These hydroxyl groups may combine to form water near 750°C as observed in the present study.

CONCLUSION

The deammoniation temperature of the washed and loaded zeolite is dependent on the oxygen partial pressure. The ammonia desorption starts in the temperature range 200-225°C and ends around 800°C in helium and around 600°C in pure oxygen. Trace nitrous oxide evolves when oxygen is present in the purge gas. Water evolves near the end of the NH_3 desorption as a reaction product of ammonia oxidation. Another water evolution peak appears at higher temperatures due to the dehydroxylation of the zeolite.

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2. Wendlandt, Z. Elektrochem., 53, 307 (1949).

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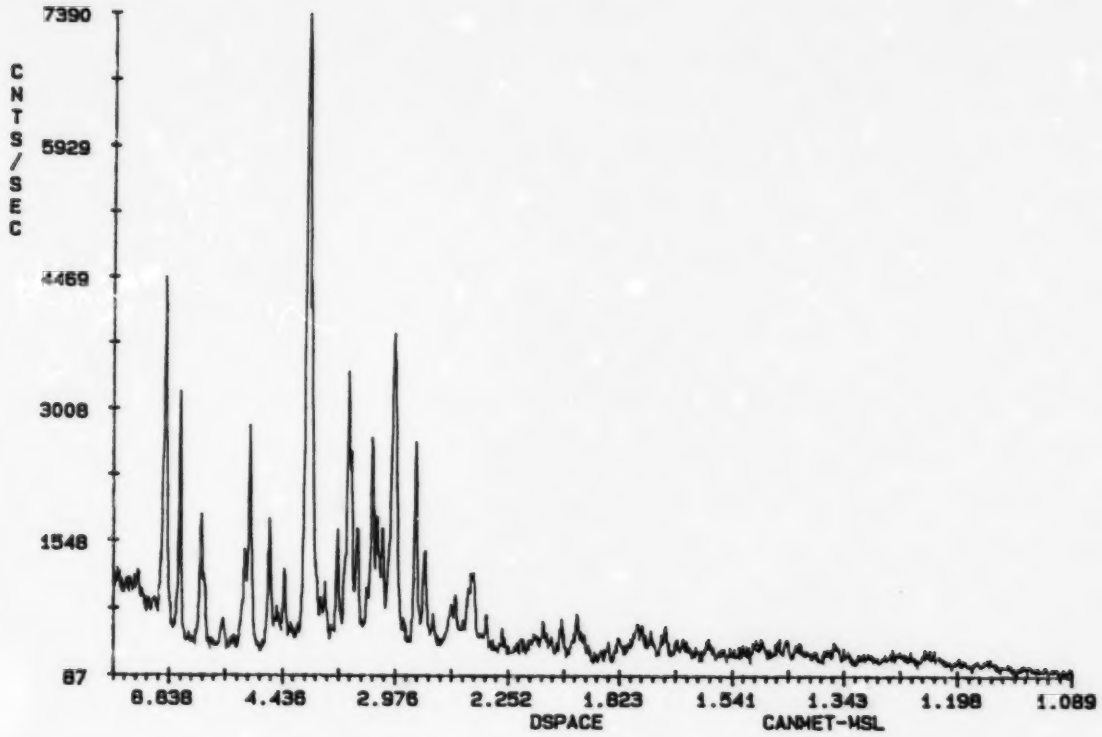

Figure 1: XRD pattern of "as received" zeolite

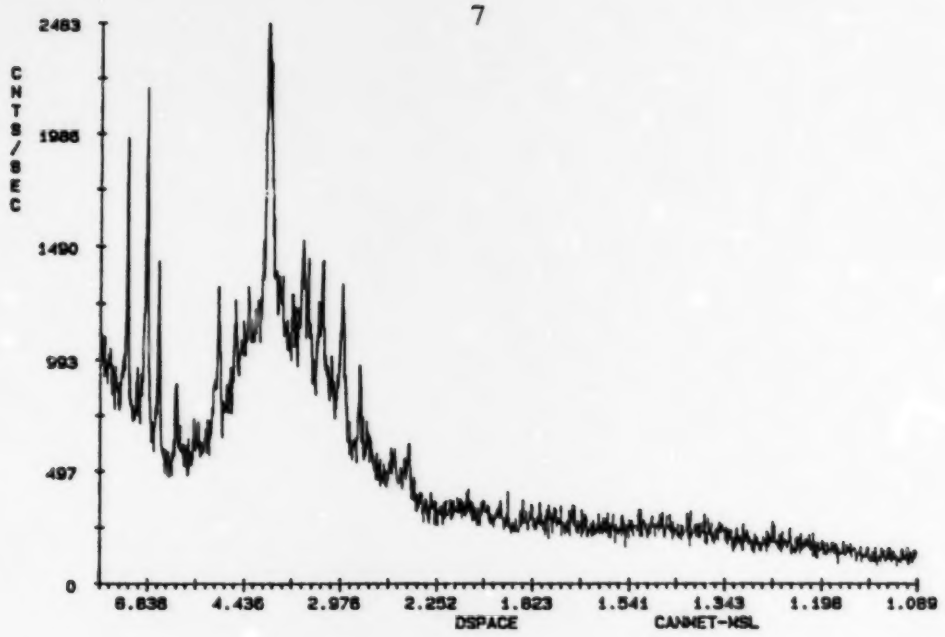

Figure 2: XRD pattern of "as received" zeolite heated to 900°C in air

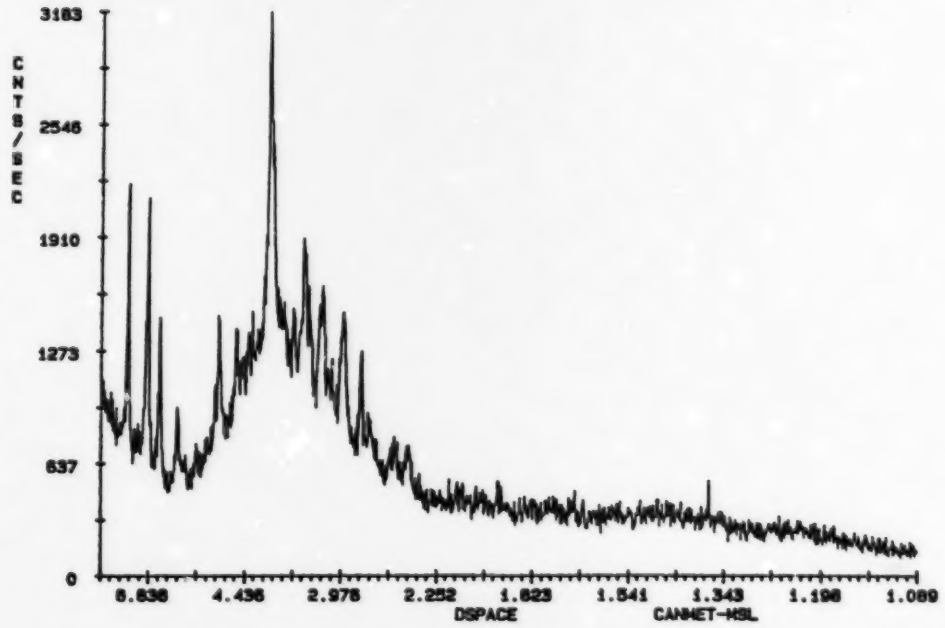

Figure 3: XRD pattern of "as received" zeolite heated to 900°C in helium

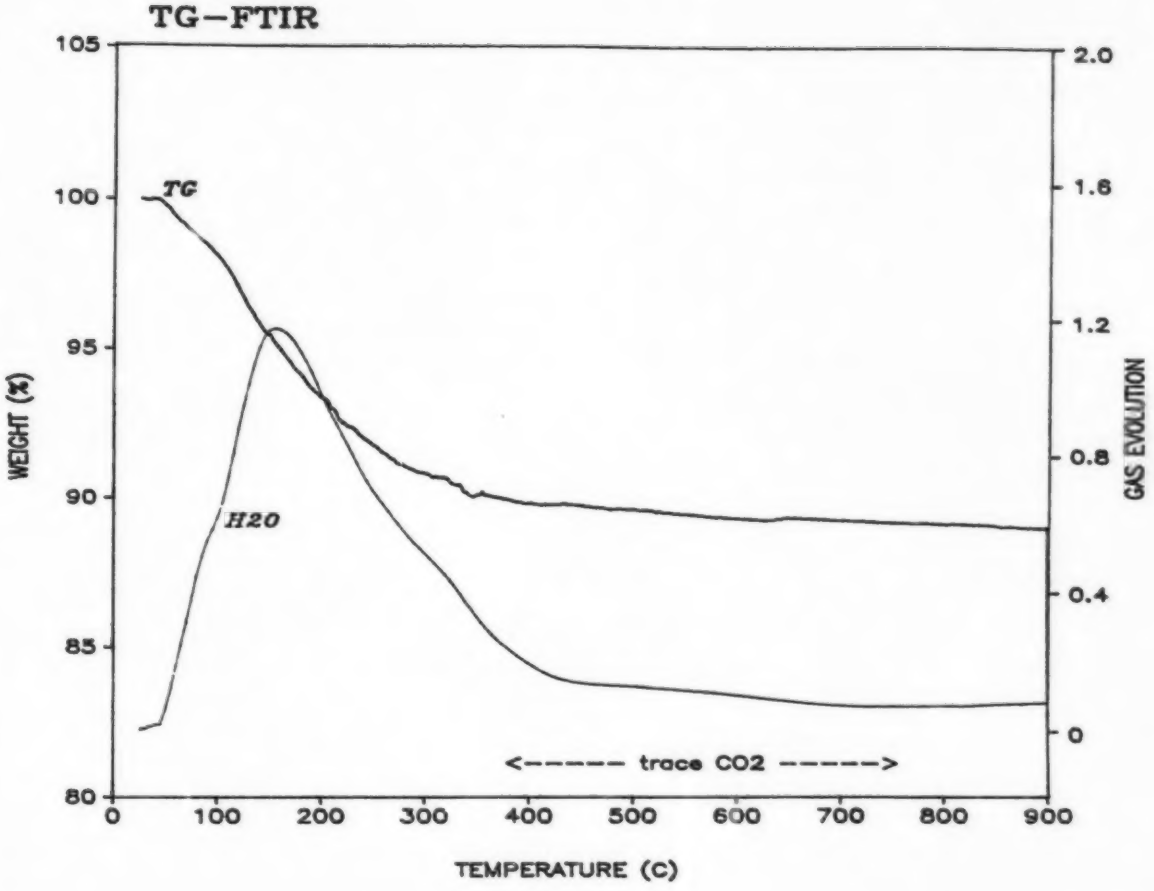

Figure 4: TG/FTIR diagrams of "as received" zeolite in helium

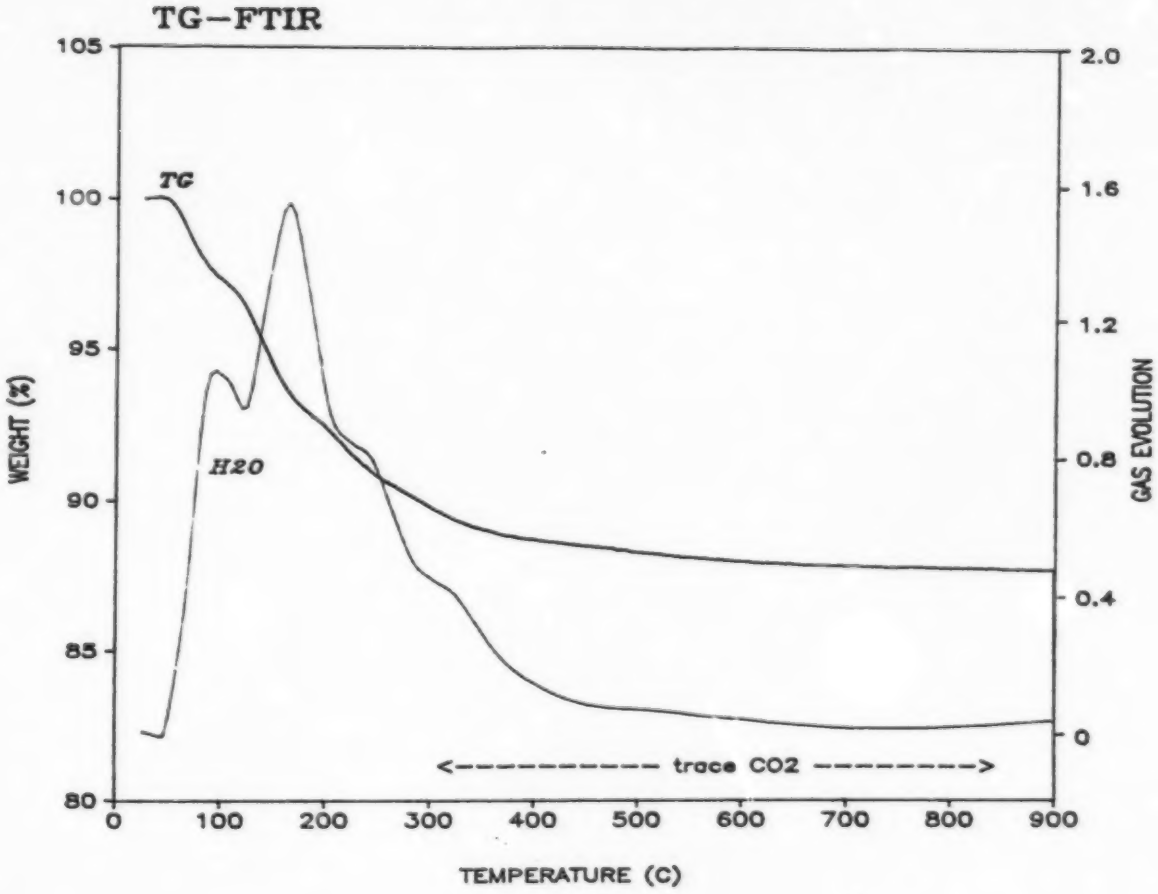

Figure 5: TG/FTIR diagrams of "as received" zeolite in helium/oxygen (1:1)

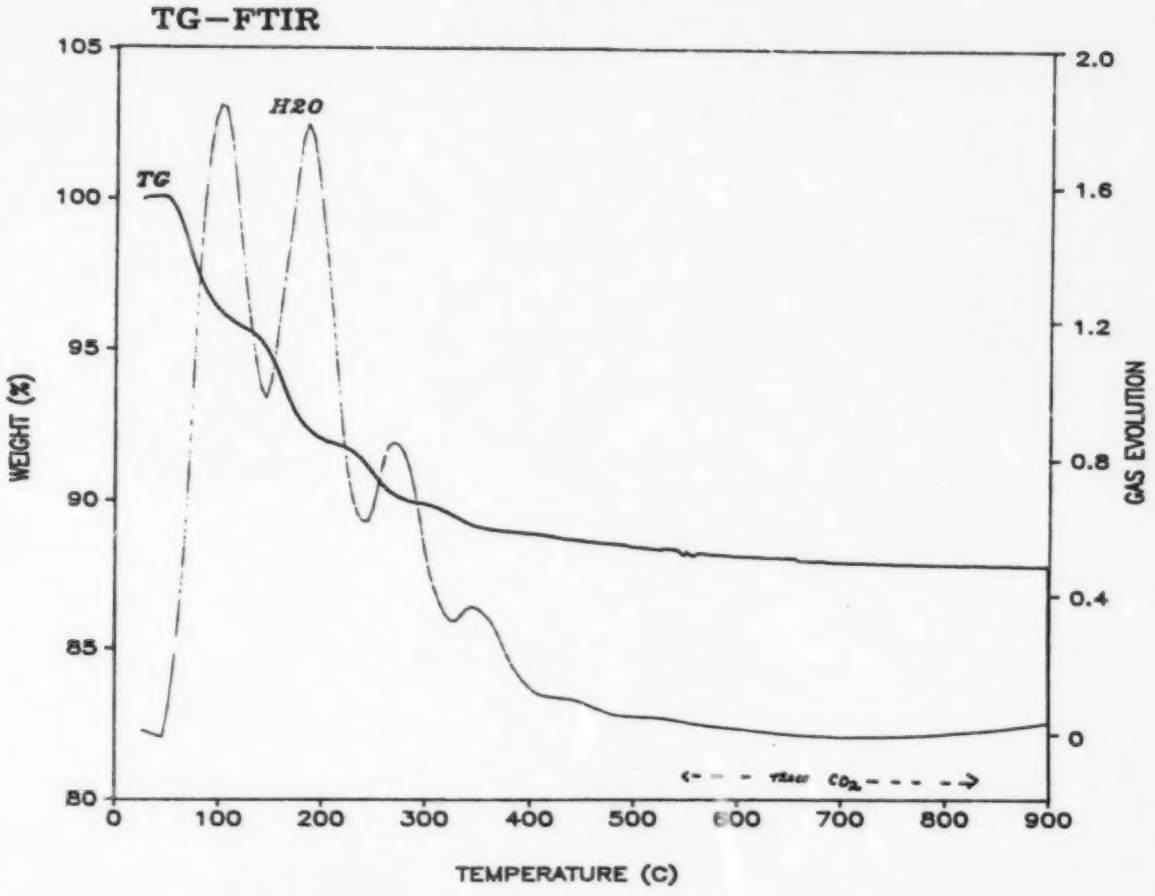

Figure 6: TG/FTIR diagrams of "as received" zeolite in oxygen

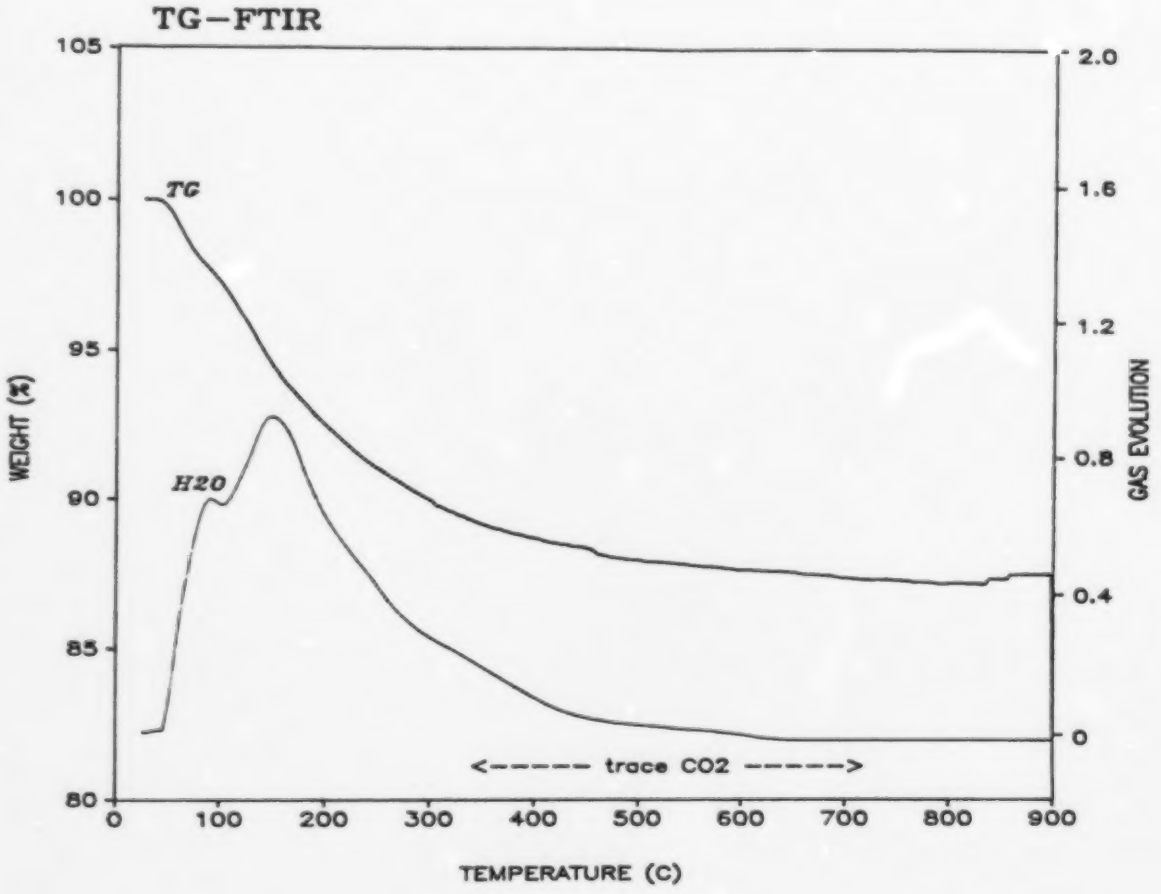

Figure 7: TG/FTIR diagrams of "washed" zeolite in helium

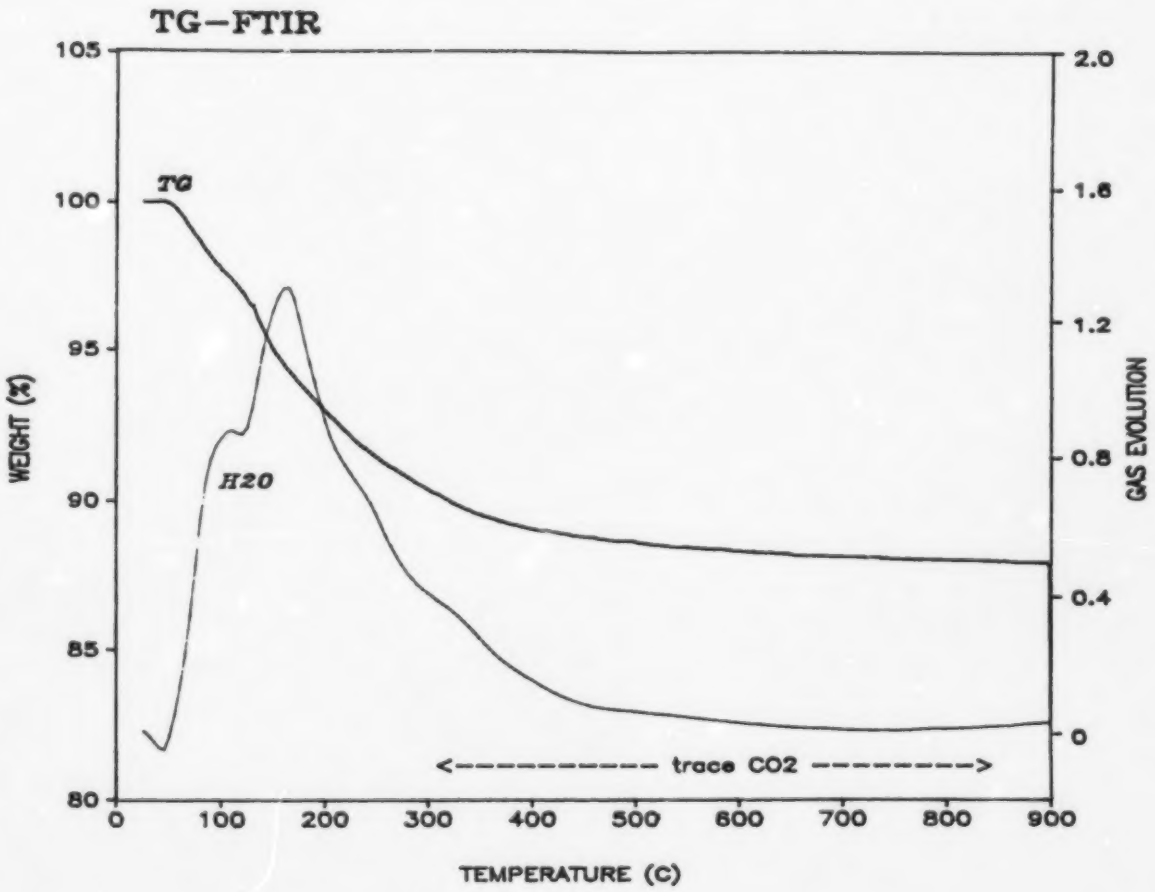

Figure 8: TG/FTIR diagrams of "washed" zeolite in helium/oxygen (1:1)

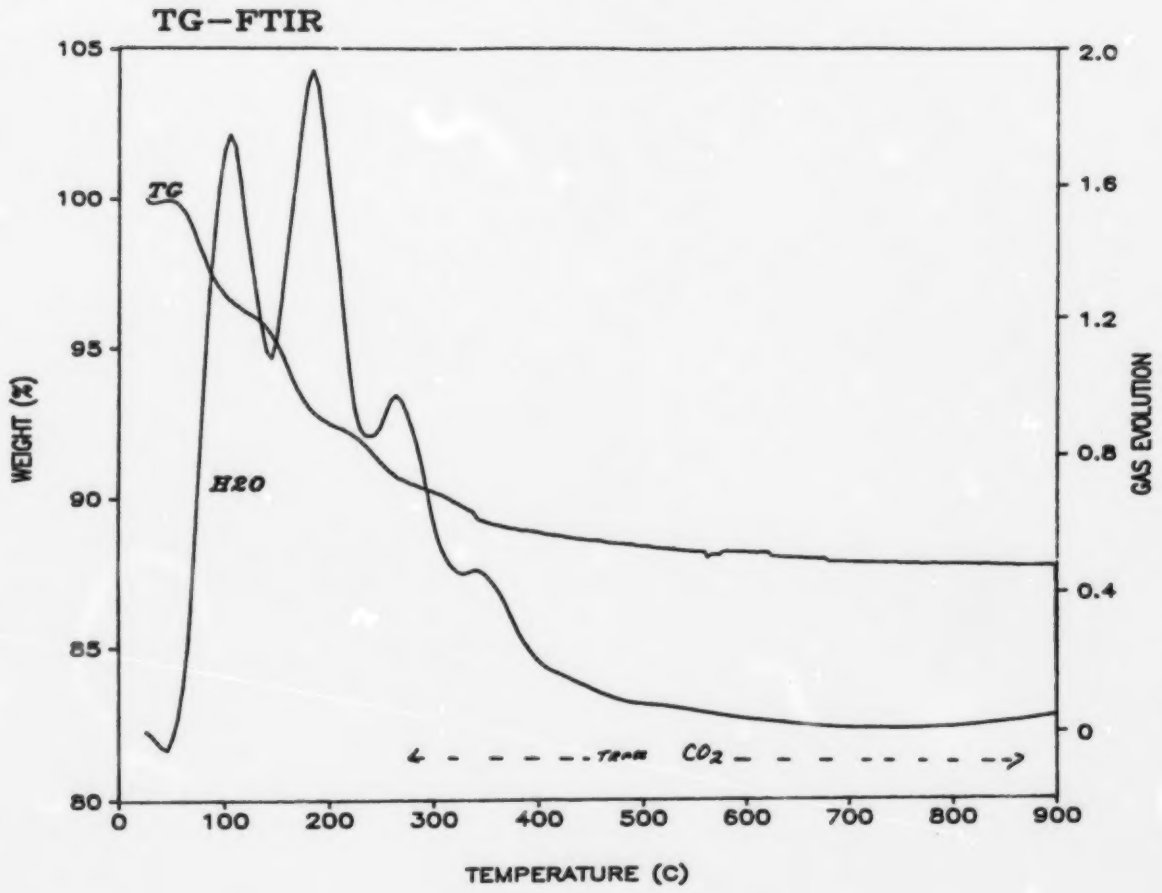

Figure 9: TG/FTIR diagrams of "washed" zeolite in oxygen

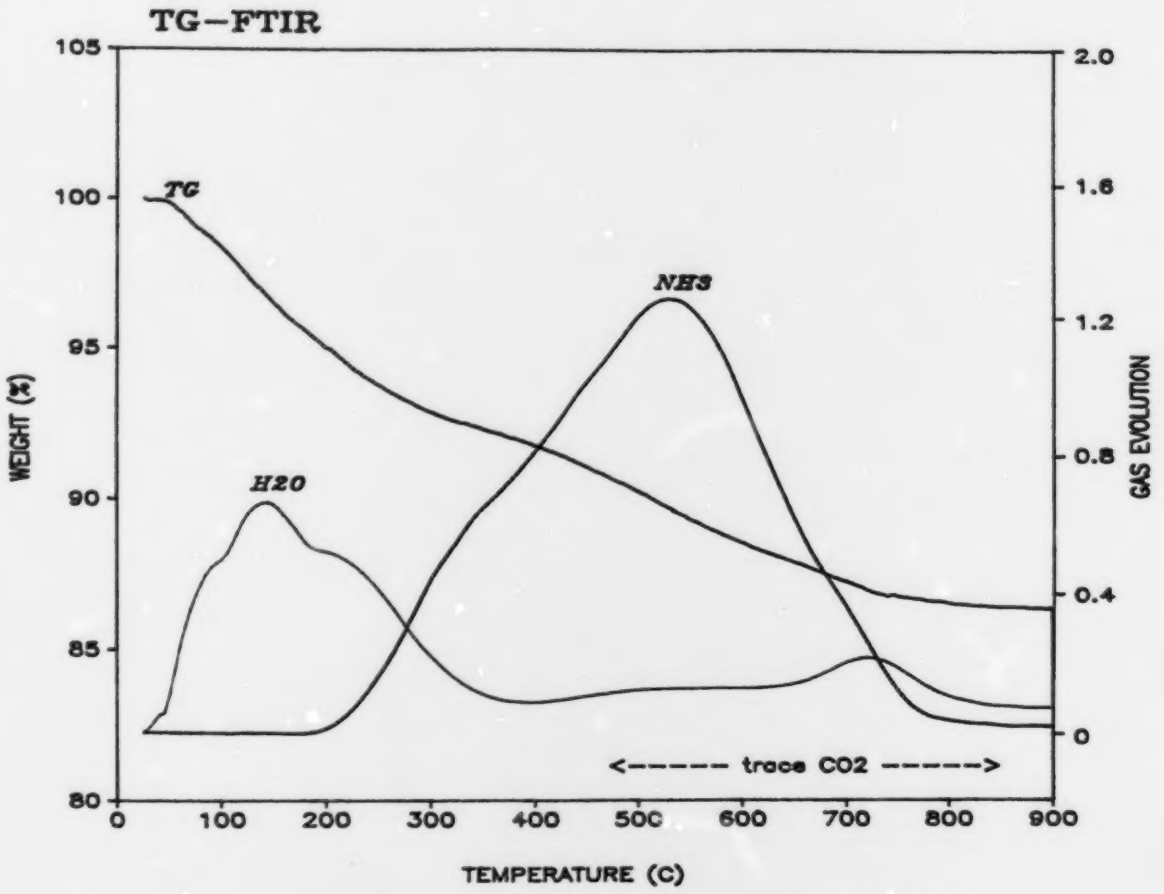

Figure 10: TG/FTIR diagrams of "washed/loaded" zeolite in helium

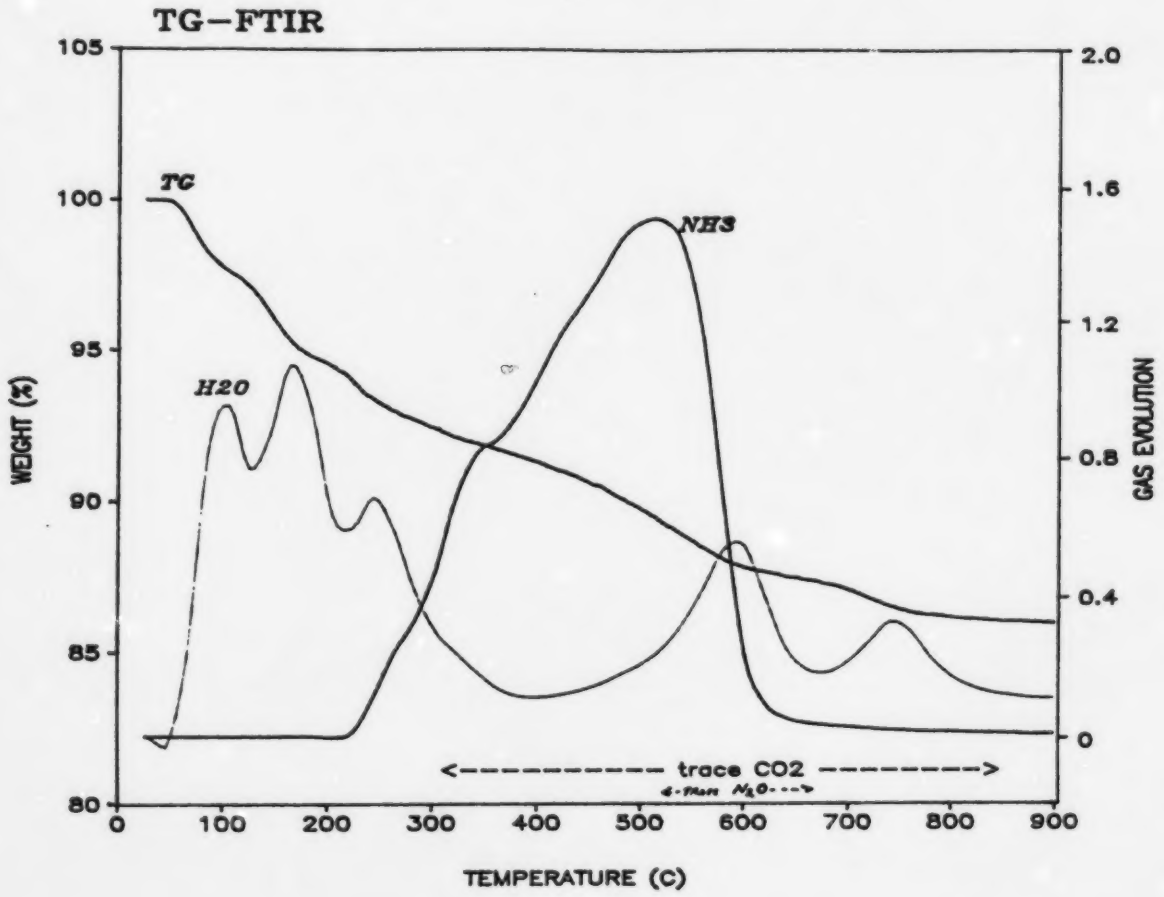

Figure 11: TG/FTIR diagrams of "washed/loaded" zeolite in helium/oxygen (1:1)

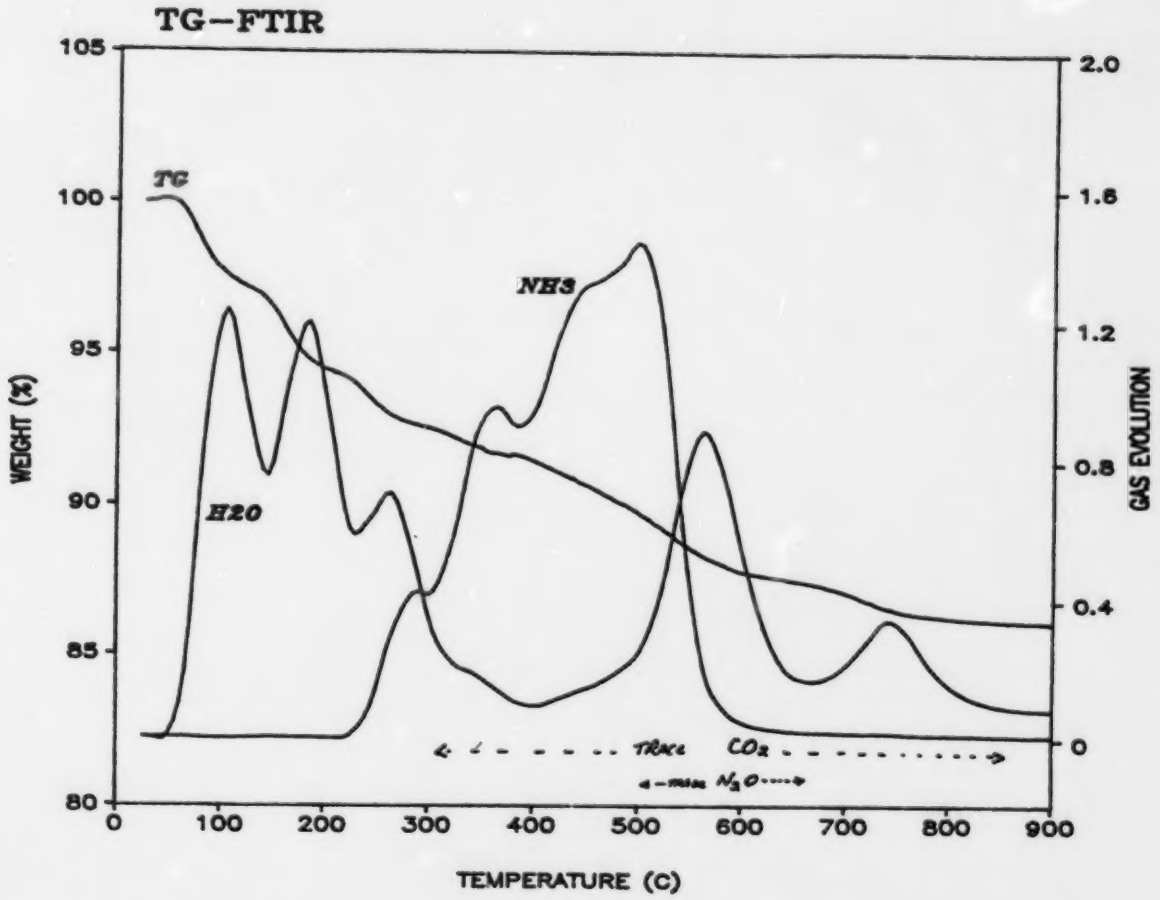

Figure 12: TG/FTIR diagrams of "washed/loaded" zeolite in oxygen

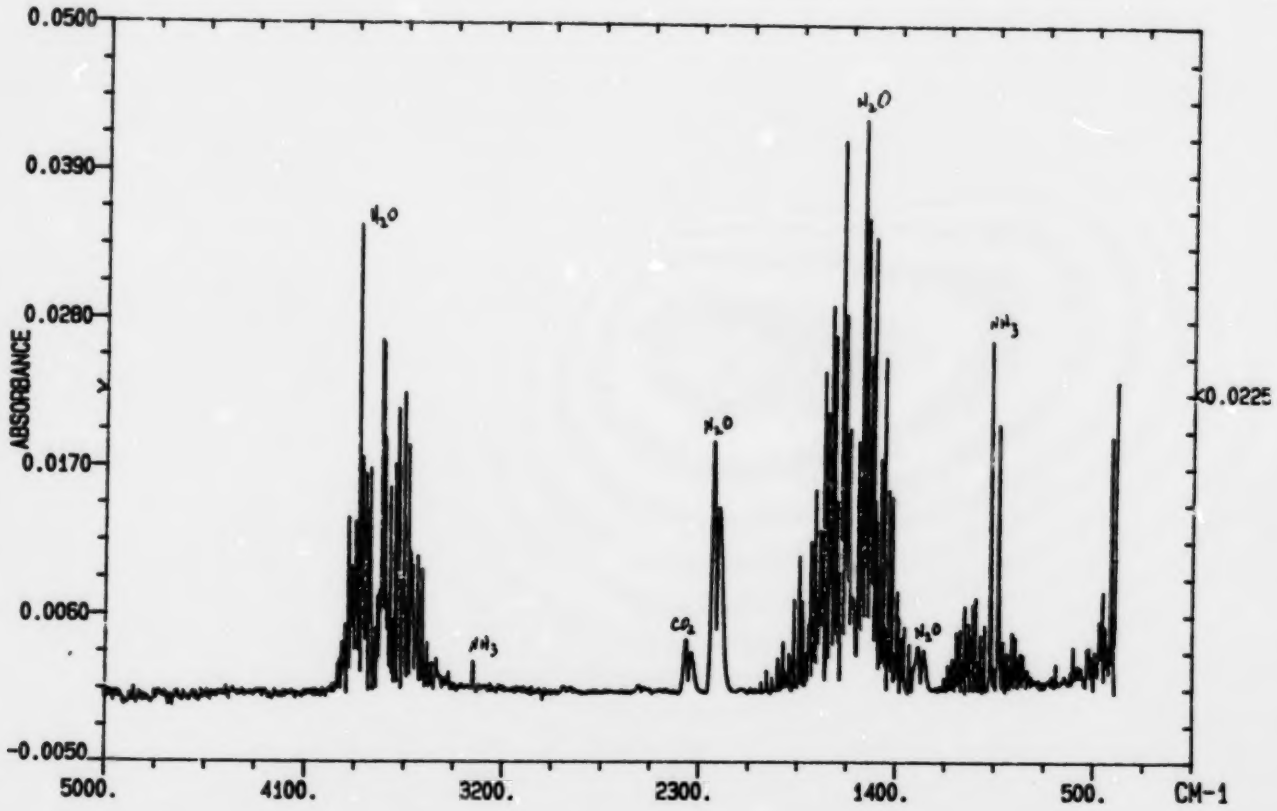

Figure 13: FTIR absorbance spectrum of gaseous species evolved from "washed/loaded" zeolite in oxygen at 550°C

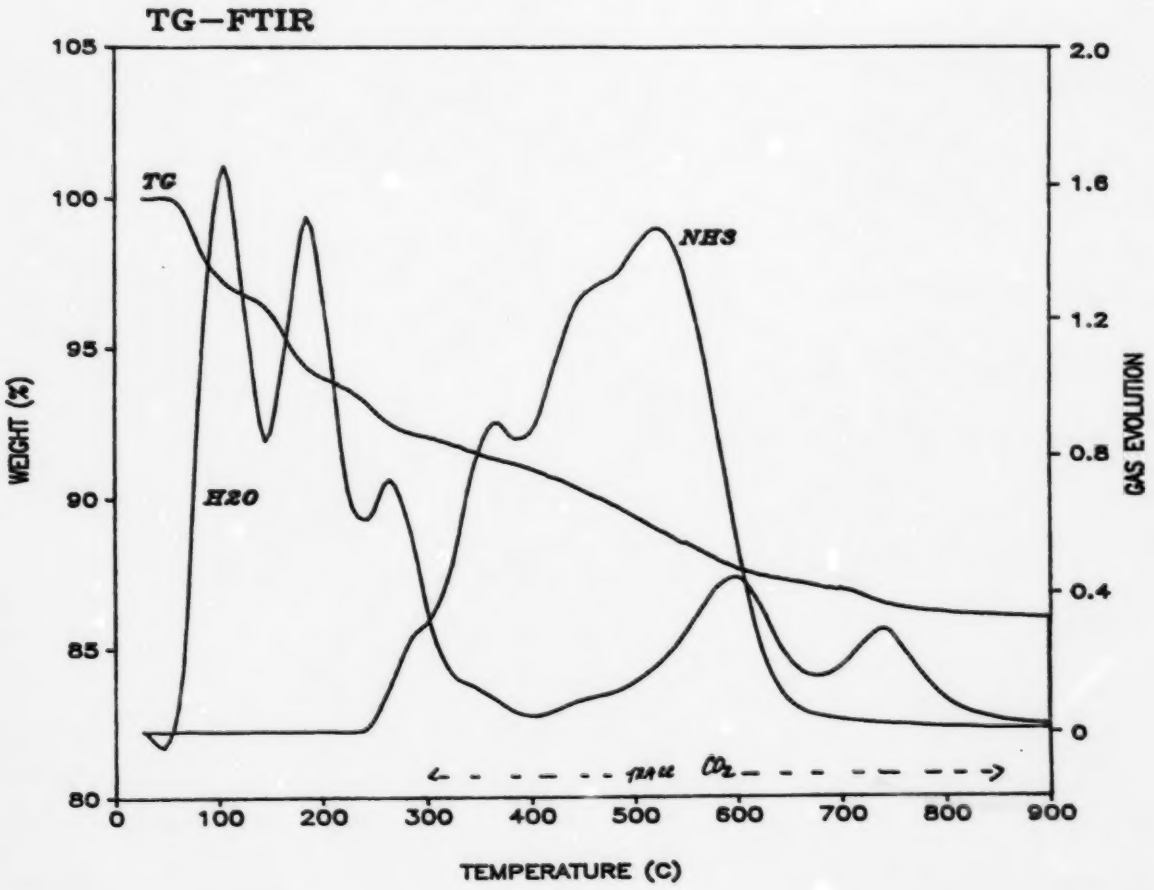

Figure 14: TG/FTIR diagram of "washed/loaded" zeolite in air